

## Energy eigenvalues and splitting between even and odd energy levels of a double-well potential

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**Abstract** : Accurate eigenvalues and splitting  $\Delta E$  between the even and odd energy levels are calculated for a double-well potential  $V(x, Z_T^2, \lambda) = -Z_T^2 x^2 + \lambda x^4$ , in the one-dimensional system, using finite difference technique for various values of parameters  $Z_T^2, \lambda$ .

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### 1. Introduction

The double-well potential for one-dimensional quantum system has been the subject of intensive study in the last two decades. The literature on this topic, voluminous as it is, has recently been thoroughly referenced by several workers [1–10].

There is a large number of physical and chemical systems whose properties can be studied (modelled) assuming that the potential function responsible for such properties is well represented by means of a function with two valleys and a barrier between them.

Some of the problems to which the double-well potential model has been applied are the interpretation of the infrared spectra of the  $\text{NH}_3$  molecule, infrared and Raman spectra of hydrogen-bonded systems, inversion characteristics of isomers, structural phase transitions, formation of noble-gas monolayers on a graphite substrate, macroscopic quantum coherence in superconducting Josephson devices, and so on [11,12]. In the theory of these problems, the most important characteristics are related to the separation between the two lowest-lying energy levels as it defines the tunnelling rate through the double-well barrier.

The fundamental system of interest to us here is the double-well potential described by Schrödinger equation

$$-\frac{d^2\Psi(x)}{dx^2} + V(x; Z_x^2, \lambda)\Psi(x) = E\Psi(x), \quad (1)$$

where  $V(x; Z_x^2, \lambda) = -Z_x^2 x^2 + \lambda x^4.$  (2)

The potential  $V(x; Z_x^2, \lambda)$  consist of two potential wells separated by a barrier. If the barrier were impenetrable to a particle, there would be energy levels corresponding to the motion of the particle in one or other well, the same for both well. The fact that a passage through the barrier is possible, results in splitting of each of these levels into two neighbouring ones, corresponding to states in which the particle moves simultaneously in both wells

The eigenvalue spectrum of the Schrödinger eq. (1) with the potential  $V(x; Z_x^2, \lambda)$  has the feature that the lower eigenvalues are closely bunched in one group if the values of the  $Z_x^2$  are sufficiently large. As  $Z_x^2$  increases, the magnitude of the splitting between the even and odd energy levels decreases.

In the present work, we have carried out a detailed investigation of the energy eigenvalues of double-well potential over a wide range of  $Z_x^2$  and  $\lambda$  values. We have achieved our objective using the finite difference. The specific goal we set before us is, to study the splitting between the even and odd energy levels over a wide range of  $Z_x^2$ ,  $\lambda$  and  $n_1$ . It is worth noting here that the finite difference technique is used in this work in the form of combination with a matrix diagonalization for numerical computations and transformed the Schrödinger equation into an algebraic eigenvalue problem.

## 2. Formulation of the finite difference method

The theory of the finite difference approach to find eigenvalues for the Schrödinger equation with potential given by eq. (2) usually starts from the central difference operator, which can be expressed as

$$\delta = e^{hD/2} - e^{-hD/2} = 2\sinh(hD/2) \quad (3)$$

from eq. (3), it is easy to get

$$h^2 D^2 = 4 \left[ \sinh^{-1} \left[ \frac{\delta}{2} \right] \right]^2, \quad (4)$$

where 
$$\sinh^{-1} \left[ \frac{\delta}{2} \right] = \left[ \frac{\delta}{2} \right] \left( 1 - \frac{1}{6} \left[ \frac{\delta}{2} \right]^2 + \frac{3}{40} \left[ \frac{\delta}{2} \right]^4 - \frac{5}{112} \left[ \frac{\delta}{2} \right]^6 + \frac{35}{1152} \left[ \frac{\delta}{2} \right]^8 + \dots \right). \quad (5)$$

Therefore, eq. (4) takes the following form

$$h^2 D^2 = \delta^2 - \frac{\delta^4}{12} + \frac{\delta^6}{90} - \frac{\delta^8}{560} + \frac{\delta^{10}}{3150} - \frac{407\delta^{12}}{24772608} + \frac{493\delta^{14}}{308281344} - \frac{25\delta^{16}}{150994944} + \frac{1225\delta^{18}}{86973087744}, \quad (6)$$

where  $h$  is the considered step length and  $\delta$  applies on function  $\Psi(x)$  as follows. Our results show involving the fourth term in eq. (6). The accuracy improves by truncating (6) after the fourth term, giving an overall accuracy of nineteen significant digits.

$$\delta\Psi(x) = \Psi\left(x + \frac{1}{2}h\right) - \Psi\left(x - \frac{1}{2}h\right), \quad (7)$$

$$\delta^2\Psi(x) = \Psi(x+h) - 2\Psi(x) + \Psi(x-h), \quad (8)$$

$$\delta^4\Psi(x) = \Psi(x+2h) - 4[\Psi(x+h) + \Psi(x-h)] + 6\Psi(x) + \Psi(x-2h), \quad (9)$$

$$\delta^2\Psi(x) = \Psi(x+3h) - 6[\Psi(x+2h) + \Psi(x-2h)] + 15[\Psi(x+h) + \Psi(x-h)] - 20\Psi(x) + \Psi(x-3h), \quad (10)$$

$$\delta^8\Psi(x) = \Psi(x+4h) - 8[\Psi(x+3h) + \Psi(x-3h)] + 28[\Psi(x+2h) + \Psi(x-2h)] - 56[\Psi(x+h) + \Psi(x-h)] + 70\Psi(x) + \Psi(x-4h). \quad (11)$$

Although the solutions of (1) are explicitly defined in  $(-\infty, +\infty)$ , it should be noted that these solutions are either of even or odd parity *i.e.*  $\Psi(x) = \pm\Psi(-x)$ , so that the determination of  $\Psi(x)$  can be restricted to the region  $(0, +\infty)$ . Furthermore, one can suppose that the wavefunctions are restricted to obey the Dirichlet boundary condition  $\Psi(x) = 0$  at some  $x$  value  $R$ . An acceptable  $R$ -value will be guessed numerically.

If we replace  $D^2$  from eq. (6) and using eqs. (7–11), the Schrödinger equation transforms into an algebraic eigenvalue problem of the form

$$[C_{m,n} - G] \Psi(nh) = 0, \quad (12)$$

where  $G$  is proportional to  $E$  and its value  $G = -5040 Eh^2$ ,  $I$  is the unity matrix. The form of matrix associated with eq. (12) can be expressed as



To solve the algebraic eigenvalue problem for eq. (12), we first transform the matrix  $C_{m,n}$  to a symmetric one. Due to the already special form of  $C_{m,n}$  this can be done by means of one similarity transformation. We then reduce this matrix to a tridiagonal form by preliminary transformations. To calculate eigenvalues of this symmetric tridiagonal matrix, we use the F02BEF Subroutine of the NAG-Library [13]. To select out the correct energy we require stability of our results with respect to the small variation of  $R$  at a given value of step length  $h$ .

### 3. Results and discussion

The finite difference technique has been applied in this paper for a double-well potentials in one dimensional system. Eigenvalues for different values of  $Z_x^2$ ,  $\lambda$  and state numbers  $n_x$  are listed in the Tables 1 and 2.

**Table 1.** Ground- and first-excited state energies for a double-well potential  $V(x, Z_x^2, \lambda = 1)$ , for different values of  $Z_x^2$ .  $E_{n_x}^{ref}$  (other) represents other values.

$Z_x^2$	$n_x$	$E_{n_x}$ (present)	$E_{n_x}^{ref}$ (other)
0	0	1 060362090484182	1.0606209048 <sup>4</sup>
	1	3.799673029801394	3.7997302980 <sup>4</sup>
0.5	0	0.870017518371612	0 870017518372 <sup>4</sup>
	1	3.333779329887006	3 33377932989 <sup>4</sup>
1	0	0 657653005180715	0 657653005191 <sup>4</sup>
	1	2.834536202119304	2.83453620212 <sup>4</sup>
2	0	0.137785848188222	0.1377858481882225 <sup>5</sup>
	1	1 713027897767675	1 713027897767675 <sup>5</sup>
4	0	-1 710350450132638	-1 710350450132640 <sup>5</sup>
	1	-1.247922492066213	-1.247922492066215 <sup>5</sup>
5	0	-3.410142761239829	-3 410142761239830 <sup>5</sup>
	1	-3.250675362289235	-3 250675362289236 <sup>5</sup>
25	0	-149.219456142190888	-149 2194561421913 <sup>6</sup>
	1	-149.219456142190888	-149.2194561421910 <sup>6</sup>
50	0	-615.020090902757816	-615.0200909027576 <sup>6</sup>
	1	-615.020090902757816	-615 0200909027576 <sup>6</sup>
100	0	-2845.867880342075294	-2845 867880342076 <sup>6</sup>
	1	-2845.867880342075294	-2845.867880342076 <sup>6</sup>
200	0	-9980 005002815982695	-9980 005002815982695 <sup>7</sup>
	1	-9980.005002815982695	-9980 005002815982695 <sup>7</sup>

As suggested by the referee, comparison with the results of other methods [4–7] has been made in Tables 1 and 2. It is clear from Tables 1 and 2 that there is agreement between our results and the results produced by other methods.

In Table 1, we compare the results obtained by the present method with those obtained by other methods [4–7]. The values of the energy are calculated over a wide range of  $0 \leq Z_1^2 \leq 200$  at  $\lambda = 1$ , for the ground and first-excited state. As  $Z_1^2$  increases, the magnitude of the splitting between the energy levels for ground and first-excited state  $|E_0 - E_1|$  decreases.

In Table 2, we compare the results obtained by our method with those obtained by using power series method for two values of  $Z_x^2 = 10, 100$  and  $\lambda = 0.5, 7.5$ . Generally speaking, the agreement between our values and those of power series is very good. Some

**Table 2.** Numerical values of some energy eigenvalues for the double-well potential  $V(\lambda, Z_1^2, \lambda)$

$Z_1^2$	$\lambda$	$n_1$	Present method	Power series method
10	0.5	0	-45.5791974486965547	-45.579197448696554735
		1	-45.5791974486818590	-45.579197448681859015
		2	-36.9538380723252171	-36.953838072325217100
		3	-36.9538380677618931	-36.953838067761893054
		4	-28.6830875222325604	-28.683087522232560427
		5	-28.6830868969642709	-28.683086896964270919
		12	-1.4089110509977329	-1.408911050997732942
		13	-0.5217551377821886	-0.521755137782188664
		16	8.9976916989575165	8.997691698957516472
		17	12.5121782111944881	12.512178211194488149
		18	16.2532388098463624	16.253238809846362366
		19	20.1747735655636969	20.174773565563696984
		0	-319.2671170279540906	-319.26711702795409060
		1	-319.2671170279540906	-319.26711702795409060
		2	-291.4454394228711989	-291.44543942287119896
		3	-291.4454394228711989	-291.44543942287119896
		4	-264.1075745401302216	-264.10757454013022166
		5	-264.1075745401302216	-264.10757454013022166
		6	-237.2797814701336811	-237.27978147013368111
		7	-237.2797814701336811	-237.27978147013368111
100	7.5	8	-210.9923806353957530	-210.99238063539575303
		9	-210.9923806353957506	-210.99238063539575069
		10	-185.2808776964343650	-185.28087769643436504
		11	-185.2808776964341016	-185.28087769643410164
		24	-27.0044852236812682	-27.00448522368126821
		25	-26.9211476446426514	-26.92114764464265145
		26	-10.0772932133725591	-10.07729321337255916
		27	-8.9598963608357662	-8.95989636083576627

Table 2. (Cont'd.)

$Z_x^2$	$\lambda$	$n_x$	Present method	Power series method
		28	2.7350408154161046	2.73504081541610463
		29	8.1915969606041077	8.19159696060410771
		30	17.4123343420860030	17.41233434208600301
		31	26.2920453927462065	26.29204539274620650
		32	36.0236079545425696	36.02360795454256961
		33	46.1417178714088725	46.14171787140887259

fine points, however may be noted, as  $Z_x^2$  increases, the energy levels for states of even and odd parity become effectively degenerate *i.e.*  $E_{\text{even}} = E_{\text{odd}}$ . The splitting increases rapidly as one goes to higher levels.

To show the dependence of the results on the choice of the  $R$  value, we present in Table 3 again for  $Z_x^2 = 10$  and  $\lambda = 0.5$ , the results obtained with step length  $h = 1/20$  but

Table 3. The dependence of the results on the choice of the  $R$  value

$Z_x^2$	$\lambda$	$n_x$	$E_{n_x}$						$R$	$h$
10	0.5	1	-45.357	148	594	361	401	06	4	1/20
			-45.579	197	233	453	902	44	5	
			-45.579	197	448	681	859	01	6	
			-45.579	197	448	681	859	01	7	
			-45.579	197	448	681	859	01	8	
			-45.579	197	448	681	859	01	10	

with six different  $R$  values, *i.e.*  $R = 4, 5, 6, 7, 8$  and  $10$ . Our results in Table 3 do not change anymore whenever  $R \geq 5$ . Of course one should control for each parameters ( $Z_x^2, \lambda$ ) choice the influence of the chosen  $R$  value on the results.

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